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REACTIVE POLYMERS

XV*. POLAR POLYMERIC SORBENTS BASED ON GLYCIDYL METHACRYLATE COPOLYMERS

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SUMMARY

The basic chromatographic characteristics of a number of copolymers based on glycidyl esters of methacrylic acid have been determined. The individual samples are characterized by a broad range of specific surface areas (44–434 m^2/g) and polarities, which have been evaluated by means of modified Rohrschneider constants. The retention times of adsorbates on these polymeric sorbents are very short, though the selectivity of separation remains intact, so that they can be used at working temperatures similar to those used in gas–liquid chromatography.

INTRODUCTION

Macroporous polymeric sorbents, *e.g.* Porapak, Chromosorb, Par, Synachrom, Spheron, Tenax, etc., have been widely used in gas chromatography[1–4]. The majority of commercial polymeric sorbents are hydrophobic and non-polar, and they interact with adsorbate molecules predominantly via dispersion forces. Only a few (Porapak R, S, T and N, Chromosorb 104, 107 and 108, Spheron and Tenax[5]) can be regarded as polar sorbents, characterized also by specific interactions; their polarity, however, mostly corresponds only to that of medium-polar stationary phases. One can therefore expect further development of polymeric sorbents aimed at an increase in polarity and in the specificity of certain interactions with characteristic series of adsorbates.

This paper reports an investigation of the basic physical and chromatographic properties of a number of glycidyl methacrylate–co-ethylenedimethacrylate (GMA–co-EDMA) copolymers.

EXPERIMENTAL

Preparation of copolymers and determination of their characteristic quantities

The individual samples of macroporous copolymers were prepared by the

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suspension copolymerization of monomers under conditions described elsewhere[6]. The concentration of epoxy groups in the copolymer was determined by titrating hydrochloric acid in excess after it had reacted with the epoxy groups of glycidyl units in the pre-swollen copolymer[7]. Fractions ranging from 150 to 200 μm were used in the chromatographic measurements.

The specific surface areas of copolymer samples were determined by the nitrogen thermal desorption method[8], and evaluated by means of the BET equation. The thermal stability was determined thermogravimetrically with a DuPont apparatus in the range 25–480° at a heating rate of 10°/min. The analyses were performed under an inert nitrogen atmosphere at a flow-rate of 200 ml/min. The thermal stability is represented by the temperature of which decomposition begins.

Chromatographic measurements

Copolymer samples were conditioned prior to measurements by heating to 170° for 24 h in a stream of nitrogen at a flow-rate of 20 ml/min. The retentions of C_5–C_{10} hydrocarbons and of the Rohrschneider standards (0.1 μl injected) were measured with a Pye apparatus (Pye Unicam, Cambridge, Great Britain) with straight glass columns (120 × 0.3 cm I.D.) at 150°. The polarity of the copolymers was determined by a modified Rohrschneider procedure[9] employed for expressing the polarity of stationary phases. A sample of graphitized carbon black, Carbopack B (Supelco, Bellefonte, Pa., U.S.A.), specific surface area 87 m²/g, average pore size 11.3 nm, was chosen as a typical non-polar sorbent. Using this sorbent, the Kováts retention indices at 150° of standard compounds were determined ($I_{\text{benzene}} = 561$; $I_{\text{ethanol}} = 296$; $I_{\text{methyl ethyl ketone}} = 476$; $I_{\text{nitromethane}} = 358$; $I_{\text{pyridine}} = 547$). These values were then used to calculate the Rohrschneider constants (x', y', z', u' and s'), modified for the evaluation of the polarity of sorbents in gas–solid chromatography (GSC).

The dynamic conditions in columns packed with copolymer samples were investigated by means of the experimental determination of the dependence of the height equivalent to the theoretical plate on the linear velocity of the carrier gas. The individual terms (A, B and C) of Van Deemter's equation were calculated from experimental data[10]. The optimum values of the linear velocity of the carrier gas were calculated from the relationship $\bar{u}_{\text{optim.}} = \sqrt{B/C}$.

In the chromatographic determination of the adsorption isotherms[11], a Perkin-Elmer F-11 apparatus provided with glass spiral columns (100 cm × 0.3 cm I.D.) was used, with injected samples of hexane and ethanol in the range 0.05–1.0 μl, with a nitrogen flow-rate of 25 ml/min. The measurements were performed at 100, 125, 150 and 175°. These measurements were used to determine the symmetry of peaks defined as the ratio of the x/y intercepts cut out from the peak at 1/10 of its height by a perpendicular drawn from the top of the peak to its baseline[12].

RESULTS AND DISCUSSION

Characterization of the sorbent

Because of the reactivity of the epoxy groups, the direct use of the GMA–co-EDMA copolymers as chromatographic sorbents was not envisaged. This is also why the original aim of this investigation was a study of the surface and sorption properties of these copolymers, modified by polymer-analogous reactions. It was shown, however, that with the exception of amines and carboxylic acids, the original copolymers do not react under chromatographic conditions with other groups of compounds; on the contrary, they are sorbents possessing surprisingly good properties.

Table I shows that by varying the ratio of GMA to EDMA, copolymers can be prepared with a broad range of specific surface areas and with sufficient thermal stability. As the proportion of the cross-linking agent (EDMA) is increased, the specific surface area of the copolymer greatly increases, which in itself indicates the possibility of obtaining a number of chromatographic packings possessing various sorption properties. A change in the copolymer composition has no essential influence on the thermal stability; a somewhat higher value was observed only with sample 1 containing a large amount of the cross-linking agent. In the thermogravimetric measurement of thermal stability, a characteristic feature of these copolymers is the negligible small mass loss before the onset of decomposition. Also, in the conditioning of chromatographic columns packed with such copolymers there are only insignificant mass losses and small volume contractions. Unlike the majority of polymeric sorbents, the composition of which is controlled only by the ratio of monomers in the copolymerization mixture, in this case it is possible to determine the proportion of GMA in copolymer, and thus the total composition.

TABLE I

BASIC CHARACTERISTICS OF MACROPOROUS COPOLYMERS GMA-co-EDMA

Grain size of samples 150–200 μm.

Sample number	*GMA in copolymer (%, w/w)*	*Specific surface area (m^2/g)*	*Thermal stability (°C)*
1	3	434	223
2	21	197	212
3	44	130	210
4	55	69	213
5	71	44	207

Chromatographic properties

The relative retention volume values of compounds of various composition (Fig. 1) indicate an increase in the specific interactions of polar compounds with increasing GMA content in the copolymer. The relative retention volumes of hydrocarbons decrease with increasing GMA content in the order of the individual homologues, in the case of the other types of compound they increase in the order benzene ≈ methyl ethyl ketone < alcohols < nitromethane < pyridine (the values for pyridine lie beyond the range shown in Fig. 1).

The adsorption equilibria in the system adsorbate–polymeric sorbent are represented by the adsorption isotherms of hexane and ethanol (Figs. 2a and b), determined from the elution chromatograms of these adsorbates with sample 4. The isotherms are almost linear in the range investigated (injections 0.05–1.0 μl), in agreement with the high symmetry of peaks obtained in chromatographic analyses using these sorbents. Table II shows an evaluation of the symmetry of the peaks of hexane and ethanol obtained with sample 4. Although the surface of the copolymers was not treated, tailing of both non-polar and polar compounds occurred only to a very small

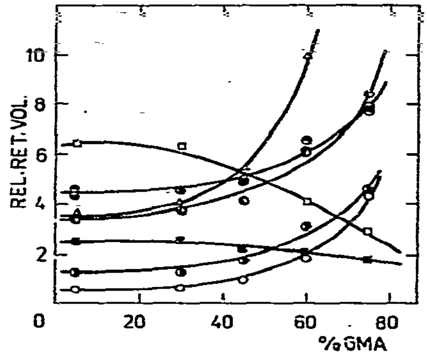


Fig. 1. The effect of the GMA content in the copolymers GMA-co-EDMA on the relative retention volumes of compounds related to the retention of pentane. Measured on glass columns (120 cm × 0.3 cm I.D.) at 150°, with an argon flow-rate of 25 ml/min. ○, Methanol; ◑, ethanol; ◐, propyl alcohol; ◒, benzene; ◓, methyl ethyl ketone; △, nitromethane; ■, hexane; □, heptane.

extent. In accordance with the adsorption isotherm, the symmetry decreases with increasing amount of the injected compound, and an increase in the working temperature leads to a considerable improvement.

The dynamic conditions in the columns packed with the copolymers were studied predominantly from the dependence of the height equivalent to the theoretical plate (H) on the linear flow-rate of the carrier gas. The experimental data were used to calculate the terms A, B and C of the Van Deemter equation[10], the optimum linear flow-rates of the carrier gas ($\bar{u}_{\text{optim.}}$) and the minimum heights equivalent to the theoretical plate ($H_{\text{min.}}$) (Table III). The negative, mainly very low values of the term A, characteristic of the majority of samples, can be regarded as zero. Owing to the spherical shape of the copolymer particles, the effect of turbulent diffusion on the separation efficiency can be neglected. This is why these sorbents need not be used in very small grain sizes (turbulent diffusion is a function of the diameter of the

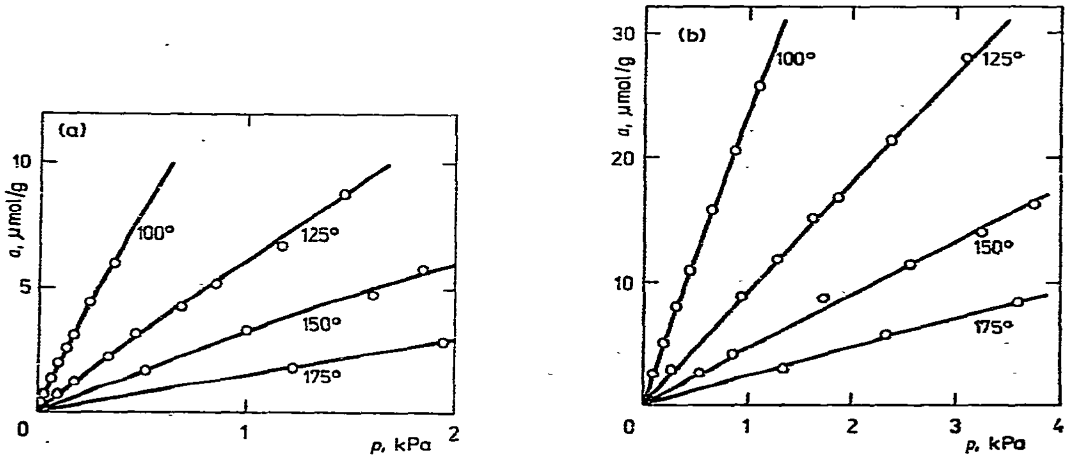


Fig. 2. Adsorption isotherms of (a) hexane and (b) ethanol on copolymer No. 4. Measured on glass columns (100 × 0.3 cm I.D.), with a nitrogen flow-rate of 25 ml/min.

TABLE II

SYMMETRY OF CHROMATOGRAPHIC PEAKS OF HEXANE AND ETHANOL, DETERMINED WITH COPOLYMER No. 4

Glass column (100 × 0.3 cm I.D.); nitrogen flow-rate 25 ml/min.

Dosage (μl)	*Hexane*				*Ethanol*			
	100°	*125°*	*150°*	*175°*	*100°*	*125°*	*150°*	*175°*
0.05	0.61	0.66	0.75	0.86	0.39	0.52	0.73	0.82
0.1	0.50	0.59	0.70	0.81	0.35	0.38	0.54	0.67
0.2	0.46	0.49	0.58	0.66	—	0.35	0.41	0.55
0.3	0.37	0.45	0.52	0.59	0.16	0.30	0.36	0.46
0.4	0.33	0.40	0.40	0.50	—	0.23	0.37	0.42
0.5	0.28	0.32	0.41	0.48	0.13	0.21	0.35	0.40
0.7	0.24	0.29	0.41	0.45	0.12	0.17	0.27	0.39
1.0	0.21	0.21	0.35	0.41	0.11	0.17	0.26	0.37

packing particles). The low values of the C term also indicate that diffusion in the pores of the sorbents and the kinetics of the adsorption–desorption process on the surface of the copolymers are sufficiently fast. The values of the B term show that the predominant influence on the peak broadening is exerted by diffusion of the sorbate molecules in the mobile phase. The high values of the terms of longitudinal diffusion (B) may be due to the lagging of those sorbate molecules that pass with the mobile phase through the bulk of the macroporous particles. The optimum flow-rates of the carrier gas are lower than those usually encountered in chromatography. The $H_{min.}$ values indicate good separation efficiency.

TABLE III

TERMS OF VAN DEEMTER EQUATION, $\bar{u}_{optim.}$ AND $H_{min.}$, CALCULATED FROM EXPERIMENTALLY OBTAINED DEPENDENCES OF H ON $\bar{u}$ FOR THE ELUTION OF PROPANOL AT 150°

Glass column (120 × 0.3 cm I.D.).

Sample number	*A (cm)*	*B (cm^2/sec)*	*C (sec)*	*$\bar{u}_{optim.}$ (cm/sec)*	*$H_{min.}$ (cm)*
1	−0.134	0.745	0.036	4.55	0.19
2	−0.020	0.285	0.015	4.36	0.11
3	−0.015	0.442	0.021	4.59	0.18
4	−0.047	0.708	0.030	4.86	0.24
5	−0.069	0.773	0.048	4.01	0.32

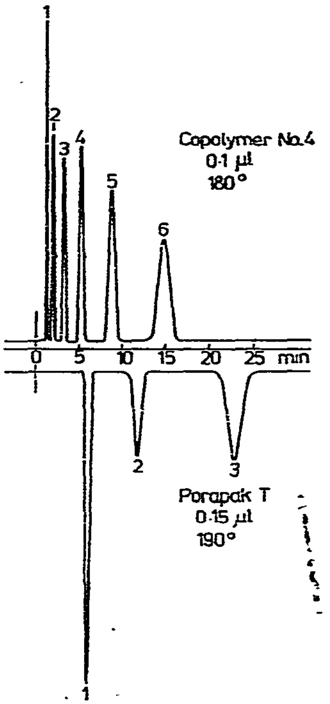
The determination of polarity of the copolymer samples was based on the Kováts retention indices of the sorbates (determined to ±0.5%), and on the Rohrschneider constants calculated from them. By substituting the retention indices of standard compounds on squalane with indices determined on Carbopack B, Rohrschneider's procedure was modified for the evaluation of the polarity of sorbents. Hence, the modified Rohrschneider constants of copolymers based on glycidyl esters (Table IV) give an additive sum of increments of all types of polar force operative in the separation of an arbitrary sorbate on the given sorbent. As can be seen in Table

TABLE IV

MODIFIED ROHRSCHNEIDER CONSTANTS CALCULATED FOR COPOLYMERS GMA-co-EDMA AND FOR COMMERCIAL MATERIALS

Glass column (120 × 0.3 cm I.D.); 150°.

Sample number	x'	y'	z'	u'	s'
1	0.98	2.33	1.89	2.81	—
2	1.05	2.37	1.89	2.92	—
3	1.40	2.80	2.24	3.54	2.75
4	2.02	3.65	2.96	4.75	3.93
5	3.58	5.05	4.38	7.24	6.04
Porapak Q	0.52	1.15	0.93	1.37	1.57
Porapak T	1.30	2.90	2.21	3.44	—



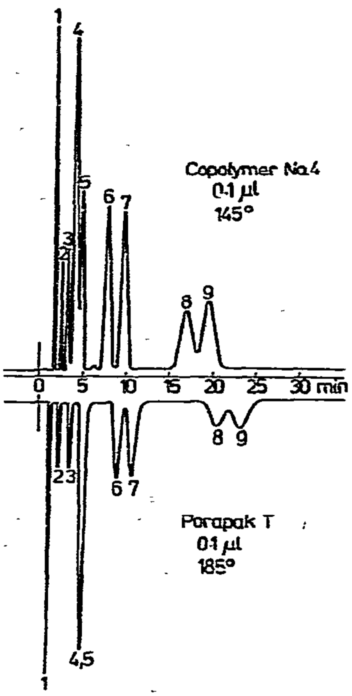
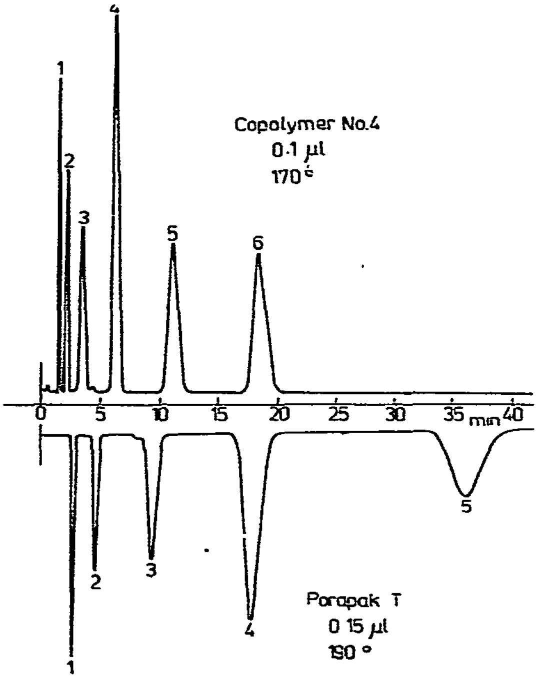


Fig. 3. The separation of a mixture of C_7–C_{12} hydrocarbons on copolymer No. 4 and Porapak T. Measured on glass columns (100 × 0.3 cm I.D.) with a nitrogen flow-rate of 27 ml/min. Peaks: 1 = heptane; 2 = octane; 3 = nonane; 4 = decane; 5 = undecane; 6 = dodecane. (Separation conditions were as shown.)

Fig. 4. The separation of a mixture of alcohols on copolymer No. 4 and Porapak T. Measured on glass columns (100 × 0.3 cm I.D.), with a nitrogen flow-rate of 29 ml/min. Peaks: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = *tert.*-butanol; 5 = propanol; 6 = isobutanol; 7 = butanol; 8 = 3-methylbutanol; 9 = pentanol.

IV, the concentration of epoxy groups in the copolymer greatly affects the polarity. The results clearly indicate that the macroporous copolymers under investigation are able to produce much stronger specific interactions with the sorbate molecules than the commercial polar sorbent Porapak T.

Consequently, in the separation of compounds on the GMA–co-EDMA copolymers, the difference in the degree of polarity of the surface becomes important, along with the different size of the specific surface. By choosing a suitable sorbent, it is possible to separate efficiently mixtures of non-polar and polar compounds. A comparison of the chromatograms of the separation on sample 4 and Porapak T of mixtures of compounds bearing various functional groups (Figs. 3–6) indicates the advantages of sorbents based on glycidyl esters. The response to a given amount of injected compound is higher, the retention times of the majority of compounds on these sorbents are considerably shorter, and the selectivity of separation is greater. Thus the working temperature can be chosen to be near the boiling points of the compounds being separated, as with GLC. This fact extends the limits of use of polymeric sorbents to include the separation of higher-boiling compounds.



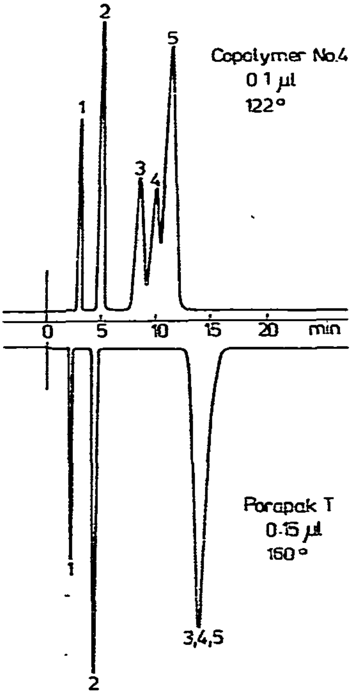


Fig. 5. The separation of acetic acid esters on copolymer No. 4 and Porapak T. Measured on glass columns (100 × 0.3 cm I.D.), with a nitrogen flow-rate of 27 ml/min. Peaks: 1 = methyl acetate; 2 = ethyl acetate; 3 = *tert.*-butyl acetate; 4 = butyl acetate; 5 = pentyl acetate; 6 = hexyl acetate.

Fig. 6. The separation of compounds with various functional groups and similar boiling points on copolymer No. 4 and Porapak T. Measured on glass columns (100 × 0.3 cm I.D.), with a nitrogen flow-rate of 29 ml/min. Peaks: 1 = methanol; 2 = ethanol; 3 = 1-chlorobutane; 4 = ethyl acetate; 5 = methyl ethyl ketone.

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